Stress–Relaxation Properties of Segmented Polyurethane Rubbers

W. DZIERŻA, *Institute of Chemistry, N. Copernicus University, Toruń, Poland*

Synopsis

Stress–relaxation behavior of polyurethane elastomers based on two hydroxyl-terminated polyesters: poly(ethylene adipate) and poly(ethylene maleate) was studied. In addition, a polyester-diol consisting of poly(ethylene adipate) and oligo(ethylene terephthalate) blocks, a number of low-molecular-weight diols as chain extenders, and 4,4′-diphenylmethane diisocyanate (MDI) were determined. The elastomers were crosslinked by an excess of MDI and had stiff segments of differing chemical structure and length. Stress–relaxation properties of the elastomers conformed with the three-component Maxwell model, with negligibly small contribution from the fastest relaxation process. The influence of crosslinking density, chemical structure, and stiff segment content on the relative relaxation speed and the parameters of the slow and fast relaxation processes, was examined. The elucidation of the results was based on the morphological models of segmented polyurethanes.

INTRODUCTION

Segmented polyurethane elastomers can be considered as crosslinked block copolymers, consisting of moderately flexible, long linear polyester or polyether segments and relatively stiff short segments comprising urethane and aromatic groups.

The practical applicability of segmented polyurethane rubbers depends on their deformational properties, resulting from the combination of segment flexibility, crosslinking, chain entanglement, orientation of segments, rigidity of aromatic units, hydrogen bonding, and other van der Waals forces.[1]

The mechanical properties of polyurethane rubbers can be extensively controlled using components of different chemical structure, at appropriate molar ratios. The deformational behavior of polyurethane elastomers are also influenced by viscoelastic effects, whose contribution depends on the chemical structure and morphology of these rubbers.

Stress–relaxation measurement is a particularly convenient static method for the investigation of viscoelasticity. It enables us to examine the processes of breaking and rebuilding polymer networks as well as changes occurring in supermolecular structures.

Stress–relaxation in polyurethanes may be conditioned by the following processes: breaking of relatively weak chemical linkages, such as urethane and allophanate,[2–4] disrupting of hydrogen and other secondary bonds,[5–7] whose concentration in polyurethanes is relatively high, and decreasing the number of free entanglements and limited slippage of trapped entanglements.[1] As a result of investigations on chemical stress–relaxation in polyurethanes, it has been found that cleavage of polymer chains occurs most readily in groups having

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nitrogen atoms.[8–16] Domain structure also exerts an essential influence on stress–relaxation behavior of urethane-block copolymers.[17–20] At temperatures below 373 K, the mechanical relaxation process occurs mainly within soft-segment domains. At temperatures above 373 K, the situation becomes more complicated because the relaxation into hard domains overlap.

The stress–relaxation in polyurethanes is most often related to the breaking of bonds of different stability. Relaxation properties in such a system conform to the multielement Maxwell model, which can be described by the relationship:

$$E(t) = \sum_{i=1}^{m} E_i(0) \exp(-t/\tau_i) \tag{1}$$

in which the observed decrease of modulus results from m degradation processes, each acting as a Maxwell element characterized by its own component $E_i(0)$ in the relaxation modulus $E(t)$, and its own constant τ_i, termed as relaxation time. For deeper characterization of the stress–relaxation behavior, one should determine parameters corresponding with respective relaxation processes taking place at a given temperature, i.e., the following pairs of constants: $E_1(0),\tau_1$; $E_2(0),\tau_2$; $E_3(0),\tau_3$, etc. The first pair of constants can be determined from the plot log $E(t)$ versus time (see Fig. 1, curve A). The straight-line segment of this curve, which corresponds with the slowest Maxwell process, is extrapolated to zero time. The intersection of the extrapolated line with the ordinate determines $E_1(0)$ value, which is a component of the initial modulus, originating from the structural elements related to the slowest relaxation process. The relaxation

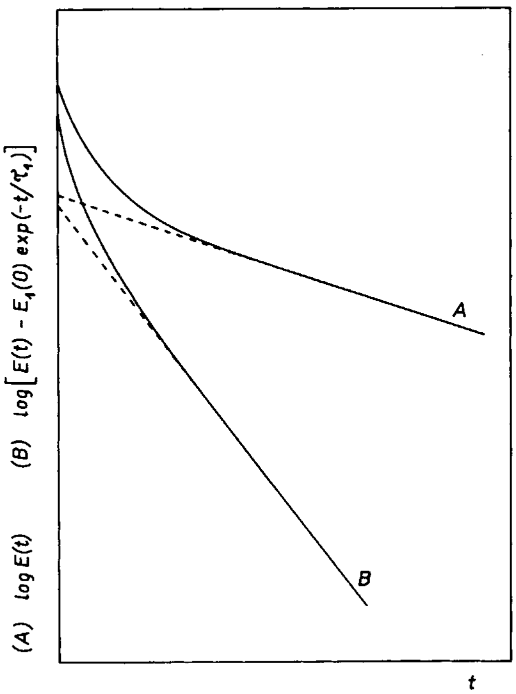

Fig. 1. Graphical determination of stress–relaxation parameters. (a) Log$E(t)$; (b) log[$E(t)$ − E_2 (0) exp(−t/τ_1)].

time, τ_1 of the slowest relaxation process can be determined from the slope of the extrapolated straight-line part of curve A. Then the relationship $\log[E(t) - E_1(0) \exp(-t/\tau_1)]$ versus time is plotted (Fig. 1, curve B), which either in part or in the whole range of time is a straight line. Repeating the extrapolation to zero time, the constant $E_2(0)$ can be evaluated. It is a component of the initial modulus related to the second slowest relaxation process. The relaxation time τ_2 is calculated from the slope of the extrapolated line. Such a procedure can be repeated to determine the parameters of rapid stress–relaxation processes occurring in a strained polymer sample.

The aim of the present study was to examine the effect of crosslinking and chemical structure as well as content of stiff segments on the stress–relaxation behavior of segmented polyurethane elastomers. There has been little interest in this problem so far, although the practical importance and application of segmented polyurethane rubbers is rapidly growing.

The elastomers studied were based on two hydroxyl-terminated polyesters: poly(ethylene adipate) (PEA) and poly(ethylene maleate) (PEM), as well as a copolyesterdiol (PEA–ET), which consisted of poly(ethylene adipate) and oligo(ethylene terephthalate) blocks at the approximate weight ratio of 4:1. As chain extenders, the following low-molecular-weight diols were used: propanediol-1,3 (PG), butanediol-1,4 (BG), triethylene glycol (TEG), polyethylene glycol-200 (PEG-200), and polyethylene glycol-600 (PEG-600). The polyaddition was conducted in the presence of 4,4′-diphenylmethane diisocyanate (MDI), whose varied excess in relation to hydroxyl end groups was to form a number of allophanate crosslinks, in addition to urethane groups, occurring in stiff short segments, linking flexible long segments of macrodiol. Stiff segments of different lengths were formed in the elastomers by using various chain extenders at varied extender-diisocyanate molar ratios.

EXPERIMENTAL

Materials

Poly(ethylene adipate), a commercial product (Poles 60/20-Chemical Works, Bydgoszcz, Poland), with hydroxyl number 58.5 and water content 0.18% was used. The number-average molecular weight, 1900, of the polyester was determined by the end-group method.

Poly(ethylene maleate) was prepared by polycondensation of maleic anhydride with ethylene glycol in the presence of p-toluenesulphonic acid as a catalyst and hydroquinone as crosslinking inhibitor.[21] The hydroxyl number of the product was 114.7, water content was 0.12%, and molecular weight 960.

Copolyesterdiol PEA–ET was obtained from Poles 60/20/20/S-Chemical Works, Bydgoszcz, Poland. The hydroxyl number of the polyester was 56.0, water content 0.24%, and the number-average molecular weight 1980, determined by the end-group method.

Propanediol-1,3 (Schuchardt, Munchen), butanediol-1,4 (Fluka AG, Buchs SG), and triethylene glycol (Union Chimique Belge, S.A.) were dried with $MgSO_4$ or $CuSO_4$ and distilled under reduced pressure.

Polyethylene glycol-200 (Carl Roth OHG) was used as received. Its hydroxyl number was 547, water content 0.09%, and molecular weight 205.

TABLE I
Chemical Characteristics of the Elastomers

Sample	Components-molar ratio	Molar ratio NCO/OH groups	MDI-crosslinker concentration mol/m^3	Content of stiff segment,[a] wt %
A1	PEA:PEM:PEG-200:MDI = 5:1:5:11.22	1.02	19.3	26.82
A2	PEA:PEM:PEG-200:MDI = 5:1:5:11.33	1.03	28.9	26.96
A3	PEA:PEM:PEG-200:MDI = 5:1:5:11.55	1.05	47.9	27.24
A4	PEA:PEM:PEG-200:MDI = 25:1:5:11.77	1.07	66.8	27.51
A5	PEA:PEM:PEG-200:MDI = 25:1:5:12.10	1.10	94.9	27.93
A6	PEA:PEM:PEG-200:MDI = 25:1:5:12.65	1.15	141	28.60
A7	PEA:PEM:PEG-200:MDI = 25:1:5:13.20	1.20	186	29.27
A8	PEA:PEM:PEG-200:MDI = 25:1:5:13.75	1.25	231	29.92
A9	PEA:PEM:PEG-200:MDI = 25:1:5:14.30	1.30	274	30.56
B1	PEA:PG:MDI = 1:1:2.2	1.10	100.6	24.80
B2	PEA:BG:MDI = 1:1:2.2	1.10	100.1	25.22
B3	PEA:TEG:MDI = 1:1:2.2	1.10	97.6	26.94
B4	PEA:PEG-200:MDI = 1:1:2.2	1.10	95.7	28.45
B5	PEA:PEG-600:MDI = 1:1:2.2	1.10	83.0	87.59

C1	PEA:TEG:MDI = 1:1:2.2	1.10	97.6	26.94
C2	PEA:TEG:MDI = 1:2:3.3	1.10	125.7	37.21
C3	PEA:TEG:MDI = 1:3:4.4	1.10	146.7	44.95
C4	PEA:TAG:MDI = 1:5:6.6	1.10	176.1	55.84
C5	PEA:TAG:MDI = 1:7:8.8	1.10	195.7	63.13
D1	PEA–ET:PG:MDI = 1:1:2.2	1.10	97.5	24.04
D2	PEA–ET:BG:MDI = 1:1:2.2	1.10	97.0	24.45
D3	PEA–ET:TEG:MDI = 1:1:2.2	1.10	94.7	26.14
D4	PEA–ET:PEG-200:MDI = 1:1:2.2	1.10	92.9	27.62
D5	PEA–ET:PEG-600:MDI = 1:1:2.2	1.10	80.9	36.63
E1	PEA–ET:TEG:MDI = 1:1:2.2	1.10	94.7	26.14
E2	PEA+ET:TAG:MDI = 1:2:3.3	1.10	122.7	36.26
E3	PEA+ET:TAG:MDI = 1:3:4.4	1.10	143.7	43.94
E4	PEA+ET:TAG:MDI = 1:5:6.6	1.10	173.6	54.82
E5	PEA+ET:TAG:MDI = 1:7:8.8	1.10	193.5	62.17

[a] The content of stiff segments formed by diisocyanate and low-molecular-weight diols calculated from the molar ratio of components.

Polyethylene glycol-600 (Schuchardt, Munchen) was used as received. Its hydroxyl number was 188 and molecular weight 594.

4-4′-Diphenylmethane diisocyanate was a commercial product (Desmodur 44, Bayer). It was purified by distillation under reduced pressure in the atmosphere of dry nitrogen, just before use for synthesis. The content of NCO groups found analytically was 33.2 wt %.

Polymerization and Preparation of Samples

The reaction of polyaddition was conducted using the one-step cast technique. A mixture of chosen components at appropriate molar ratio was poured into Teflon molds, heated at 353 K under reduced pressure for 8 h, and then cured at 426 K for 1 h.[22] The sheets of elastomers produced were approximately 12 × 9 × 0.2 cm and were cut into samples for measurements. Five series of samples (A, B, C, D, and E) were obtained. The chemical characteristics of samples are given in Table I.

In order to evaluate the changes of crosslinking density with changes of chemical composition of elastomers, the sol:gel ratio and the equilibrium volume fraction v_2 of the polymer in toluene-swollen samples were determined at 298 K. The samples of about 15 × 20 × 2-mm were swollen in toluene for several days until the equilibrium state was reached. The equilibrium volume fraction v_2 of the polymer in the swollen sample was calculated from the weights of swollen and dry samples and from the solvent and polymer densities. The calculation of v_2 was based upon the assumption of additivity of the polymer and solvent volumes. The sol:gel ratio in the elastomers was calculated from the weights of dry samples before and after swelling, where the solvent had been removed at 323 K, under reduced pressure. The results are given in Table II.

Stress–Relaxation Measurements

The measurements for stress–relaxation were conducted using an Instron tensile-testing instrument type 1026, equipped with a thermostatting jacket connected to an ultrathermostat. Strips of samples of approximately 110 × 7.4 × 2 mm were extended rapidly at a crosshead speed of 50 cm/min to an elongation of 20%. Constant strain was maintained throughout the 3-h experiment. The changing value of tensile force was recorded on a moving chart. The stress–relaxation behavior was investigated at 323 K, which was controlled within an accuracy of 0.2 K. The relaxation moduli $E(t)$ were calculated using the relationship:

$$E(t) = \delta(t)\epsilon^{-1} \tag{2}$$

where $\delta(t)$ is stress at the time t, related to the initial cross-sectional area, and ϵ is the deformation. All the values to be measured, i.e., dimensions of undeformed samples, tensile force, and strain were determined with an accuracy better than 1%. The results were plotted in different ways to evaluate the relative relaxation speed and relaxation parameters of the elastomers.

TABLE II
Swelling Characteristics of the Elastomers in Toluene at 298 K

Sample	Sol/gel ratio	v_2
A1	—	—
A2	0.316	0.088
A3	0.190	0.128
A4	0.143	0.156
A5	0.089	0.231
A6	0.069	0.294
A7	0.0526	0.341
A8	0.0417	0.406
A9	0.0307	0.469
B1	0.0723	0.373
B2	0.0752	0.370
B3	0.0758	0.366
B4	0.0806	0.365
B5	0.0842	0.350
C1	0.0758	0.366
C2	0.0687	0.390
C3	0.0520	0.437
C4	0.0438	0.468
C5	0.0323	0.535
D1	0.0684	0.361
D2	0.0721	0.352
D3	0.0753	0.347
D4	0.0769	0.341
D5	0.0792	0.332
E1	0.0753	0.347
E2	0.0690	0.385
E3	0.0607	0.413
E4	0.0529	0.445
E5	0.0438	0.494

RESULTS AND DISCUSSION

To evaluate the influence of the chemical structure and the content of stiff segments on the stress–relaxation properties of segmented polyurethane elastomers, the 10- and 100-s moduli, $E(10\ \mathrm{s})$ and $E(100\ \mathrm{s})$, were estimated and the values of $V_r = (E(10\ \mathrm{s}) - E(100\ \mathrm{s})]/E(10\ \mathrm{s})$, which can be taken as a qualitative measure of the relaxation speed, were calculated for series B, C, D, and E at 323 K. The results obtained are listed in Table III.

For rubbers of series B and D, at constant molar ratio of components, and diol chain extenders of different chamical structure and length, the $E(10\ \mathrm{s})$ and $E(100\ \mathrm{s})$ moduli decreased and the relative relaxation speed V_r increased, when the length of diols increased. These changes are caused by a slight drop in crosslinking density and by an increase in stiff segments content, whose flexibility increases as a result of increasing distance between neighboring urethane groups.

For the elastomers of series C and E, in which the crosslinking density and stiff-segment content increase to more than doubled values, as a result of an

TABLE III
Stress–Relaxation Moduli of Segmented Polyurethane Elastomers at 323 K

Sample	MDI-crosslinker conc, mol/m^3	Content of stiff segments wt %	E (10 s) MPa	E (100 s) MPa	V_r
B1	100.6	24.80	4.63	3.50	0.244
B2	100.1	25.22	4.47	3.35	0.251
B3	97.6	26.94	4.29	3.14	0.268
B4	95.7	28.45	3.96	2.88	0.273
B5	83.0	37.59	3.15	2.23	0.292
C1	97.6	26.94	4.29	3.14	0.268
C2	125.7	37.21	5.51	4.34	0.212
C3	146.7	44.95	6.38	5.29	0.171
C4	176.1	55.84	7.91	7.04	0.110
C5	195.7	63.13	8.80	8.43	0.042
D1	97.5	24.04	3.18	2.53	0.204
D2	97.0	24.45	3.04	2.40	0.211
D3	94.7	26.14	2.82	2.18	0.227
D4	92.9	27.62	2.59	1.97	0.239
D5	80.9	36.63	2.12	1.52	0.283
E1	94.7	26.14	2.82	2.18	0.227
E2	122.7	36.26	3.77	3.08	0.183
E3	143.7	43.94	4.53	4.00	0.117
E4	173.6	54.82	5.46	5.00	0.084
E5	193.5	62.17	6.04	5.96	0.013

increasing share of diol chain extender (TEG) in the components, the moduli $E(10\text{ s})$ and $E(100\text{ s})$ apparently increase, and the relative relaxation speed V_r rapidly decreases. The rapid drop of V_r values is supposedly caused by the parallel influence of crosslinking density and stiff-segment content on the disappearance of viscoelastic properties.

A comparison of results obtained for the rubbers of series B and C with those of D and E shows that elastomers produced from the copolyesterdiol PEA–ET have smaller relaxation than rubbers obtained from PEA polyesterdiol. The improvement in stress–relaxation properties of polyurethane rubbers, on the basis of copolyesterdiol results was due to increased elasticity of soft-segment domains. In the soft domains of these polyurethane elastomers, the possibility of formation of ordered structures is smaller.

In order to better characterize the stress–relaxation properties of segmented polyurethane elastomers, the relation of $\log(\delta_t/\delta_0)$ versus time was plotted for elastomers of the series A, B, and C. All the rubbers examined displayed curved-line plots, like the ones presented in Figure 2 for elastomers A2–A8. Stress–relaxation behavior of elastomers investigated does not conform to the elemental Maxwell model, but should be described by the multicomponent model in eq. (1).

Stress–relaxation of polyurethanes had initially been interpreted[9,10] on the basis of the relationship

$$E(t) = E(0)\exp(-t/\tau) \tag{3}$$

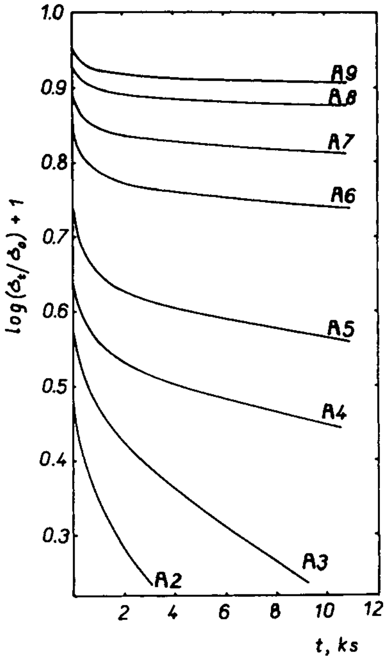

Fig. 2. Stress–relaxation in terms of $\log(\delta_t/\delta_0)$ vs. time for samples A2–A9. Temperature, 323 K.

but more precise measurements, carried out at 393 and 433 K, showed that relaxation properties of these polymers were better characterized by an expression containing the sum of two exponential functions[8,14]:

$$\delta_t/\delta_0 = A\ \exp(-t/\tau_1) + B\ \exp(-t/\tau_2) \tag{4}$$

where the constants A and B comply with $A + B = 1$.

The analysis of stress–relaxation behavior of the polyurethane rubbers was based on eq. (1). The applicability of this method for segmented polyurethane elastomers is exemplified in Figures 3 and 4. The plots of $\log[E(t) - E_1(0)$

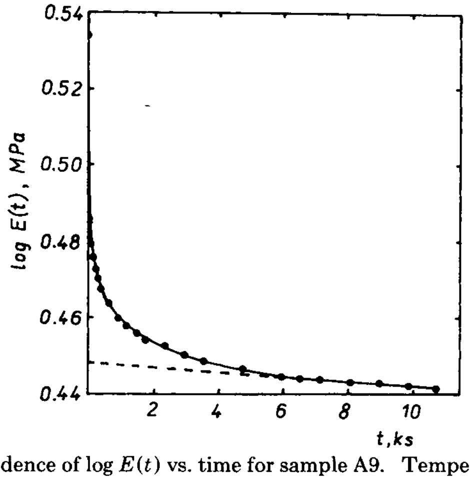

Fig. 3. Dependence of log $E(t)$ vs. time for sample A9. Temperature, 323 K.

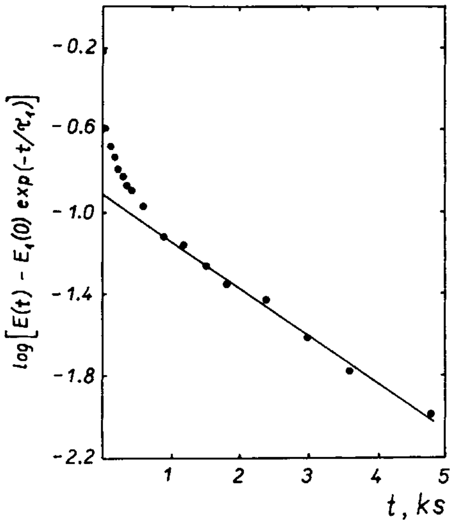

Fig. 4. Dependence of $\log[E(t) - E_1(0)\exp(-t/\tau_1)]$ vs. time for sample A9. Temperature, 323 K.

$\exp(-t/\tau_1)]$ versus time have proved that stress–relaxation properties of these rubbers conform to the three-component Maxwell model, but at the same time, the contribution of the fastest process to the overall drop of relaxation modulus is very small. The values of stress–relaxation parameters of the two main constituent processes for the samples of the A, B, and C series, computed using the least-squares method, are listed in Table IV. The values for overall relaxation time τ_g, were estimated from plots of $E(t)$ versus time. Since the stress–relaxation properties of the polyurethanes examined do not conform to the elemental Maxwell model, the value of τ_g can only be considered as a convenient empirical parameter, characterizing mechanical stability of the system.

The elastomers A1–A9 of the slow relaxation process, which is characterized by τ_1 and $E_1(0)$ parameters, apparently depend on crosslinking density (See Table IV). With the increase of MDI-crosslinker concentration from about 20 to 270 mol/m^3, the value of τ_1 increases by almost two orders and the $E_1(0)$ component value of the relaxation modulus also displays a great increase. In contrast, the speed of the fast relaxation process is not influenced by crosslinking density and the parameter τ_2 is approximately constant. On the other hand, the parameter $E_2(0)$ increases, but only by about one order in the range of the MDI-crosslinker concentration examined. The overall relaxation time, τ_g, for the elastomers A1–A9 displays an exceptionally large increase with an increase in crosslinking density. This is a result of a rapid drop of $E(t)$ modulus at the very beginning of the stress–relaxation experiments, which features the elastomers of low crosslinking density.

In the series D1–D5, in which MDI-crosslinker concentration slightly diminishes and the stiff-segment content increases due to the application of diol extenders of increasing length, the parameters τ_1 and $E_1(0)$ of the slowest relaxation process and the overall relaxation time, τ_g, decrease (Table IV). In contrast, the relaxation time, τ_2, of the rapid process is not influenced by these variables and the parameter $E_2(0)$ slightly diminishes.

TABLE IV
Stress-Relaxation Parameters of Segmented Polyurethane Elastomers at 323 K

Sample	MDI-crosslinker conc, mol/m^3	Content of stiff segments, wt %	τ_g, ks	τ_1, ks	τ_2, ks	E_1 (0) MPa	E_2 (0), MPa
A1	19.3	26.82	0.0168	14.8	1.82	0.041	0.0134
A2	28.9	26.96	0.0300	24.5	1.73	0.069	0.0208
A3	47.9	27.24	0.120	55.2	1.92	0.103	0.0363
A4	66.8	27.51	1.44	85.8	1.91	0.270	0.0527
A5	94.9	27.93	11.2	113	1.57	0.487	0.0670
A6	141	28.60	17.9	124	1.78	0.955	0.0840
A7	186	29.27	24.9	235	1.94	1.42	0.0971
A8	231	29.92	38.3	494	1.67	2.07	0.109
A9	274	30.56	50.8	722	1.88	2.81	0.123
B1	100.6	24.80	18.1	234	2.73	3.06	0.572
B2	100.1	25.22	15.6	158	2.48	2.93	0.563
B3	97.6	26.94	13.8	96.2	2.32	2.71	0.558
B4	95.7	28.45	9.72	51.4	2.66	2.34	0.541
B5	83.0	37.59	2.08	18.5	2.51	1.67	0.517
C1	97.6	26.94	13.8	96.2	2.32	2.71	0.558
C2	125.7	37.21	29.3	173	2.41	3.74	0.577
C3	146.7	44.95	42.7	402	2.33	5.32	0.631
C4	176.1	55.84	59.5	738	2.80	6.47	0.670
C5	195.7	63.13	73.4	1220	2.57	7.98	0.739

For the elastomers of the C1–C5 series, in which crosslinking density and stiff-segment content rises, an apparent increase in the relaxation parameters τ_1 and $E_1(0)$ of the slowest process, as well as the overall relaxation time τ_g, can be observed. The relaxation time τ_2 of the fast process, as in series A1–A9 and B1–B5, depend neither on crosslinking density nor on stiff-segment content, while the parameter $E_2(0)$ increases slightly with an increase in the variables.

Segmented polyurethane elastomers are complex in chemical structure, and it is difficult to explain what molecular motions are responsible for a particular relaxation process. Apart from physical relaxation processes, chemical relaxation, due to poor stability of some linkages such as allophanate or urethane, may also occur, depending on experimental conditions. Physical stress–relaxation of polyurethanes may be based on several mechanisms,[23] and the disruption of secondary bonds is a crucial factor. This results in some structural changes within hard and soft domains. The disappearance of cohesion in the hard domains may result from the rise in temperature, applied stress, or repeated strain, which lead to softening of the polymer and an increase in stress–relaxation.

On the basis of morphological models of polyurethanes proposed in the literature,[24–28] the slow relaxation process, which depends on crosslinking density, is connected with the orientation of hard domains. The fast relaxation process might be related to the disruption of chemical and secondary bonds.

A more reliable explanation for the mechanism of stress–relaxation in segmented polyurethane rubbers, will be possible after completing stress–relaxation measurements under various experimental conditions, particularly at different strains, strain rates, and at considerable temperature ranges.

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